

Oxidation products and pathway of ceramic honeycomb-catalyzed ozonation for the degradation of nitrobenzene in aqueous solution

Lei Zhao ^{a,*}, Jun Ma ^{a,**}, Zhi-zhong Sun ^b

^a School of Municipal and Environmental Engineering, Harbin Institute of Technology, P.O. Box 2627,
202 Haihe Road, Harbin 150090, People's Republic of China

^b College of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, People's Republic of China

Received 9 February 2007; received in revised form 10 October 2007; accepted 22 October 2007
Available online 30 October 2007

Abstract

Semi-continuous experiments on catalytic ozonation of nitrobenzene (NB) in aqueous solution using ceramic honeycomb as catalyst have been investigated. Experimental results showed that the presence of ceramic honeycombs significantly increased the ozonation degradation rate of NB compared to the case of non-catalytic ozonation. With addition of the radical scavenger *tert*-butanol, the evident reduction of NB removal indicated that NB was oxidized primarily by hydroxyl radical ($\cdot\text{OH}$) in the both systems of ozonation alone and ozonation/ceramic honeycomb. The total organic carbon removal suggested that in the process of ozonation/ceramic honeycomb NB was more quickly mineralized than that by ozonation alone. The absorbance of UV-vis spectra confirmed that carboxylic acids and aromatic compounds were predominant oxidative organic products of NB by catalytic ozonation. The oxidative decomposition products (*o*-, *p*-, *m*-nitrophenols, phenol, 4-nitrocatechol, hydroquinone, *p*-quinone, 1,2,3-trihydroxy-5-nitrobenzene, maleic acid, malonic acid, oxalic acid, acetic acid and nitrate ion) have been identified by GC/MS and IC, indicating that degradation proceeded via $\cdot\text{OH}$ oxidation. A general reaction pathway for the degradation of NB was proposed by the evidence presented in this study.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Catalytic ozonation; Ceramic honeycomb; Nitrobenzene; Decomposition products; $\cdot\text{OH}$

1. Introduction

Nitrobenzene (NB), a carcinogenic pollutant [1], is one of the fastest-growing end-use synthetic products of benzene [2], such as dyes [3,4], plastics, explosives, pharmaceuticals [5] and pesticides [6]. NB has been used to produce aniline and, as an organic solvent, has been widely dispersed in water and soil, causing great environmental concern because of its toxicity, quantity of production and difficult biodegradation, even at low concentrations [7–11]. The strong electron-withdrawing property of the nitro-group of NB resists to oxidation by biological treatment and conventional chemical oxidation [1,3,12–16]. Furthermore, NB and some of its transformation metabolites,

such as nitrosobenzene, hydroxylaminobenzene and aniline, exhibit toxic and mutagenic effects on biological systems [17–20]. Therefore, exploration of effective methods for NB degradation represents an important research challenge and various alternative treatment technologies have been developed over the last two decades in order to cost-effectively meet environmental regulatory requirements, some of which are advanced oxidation processes (AOPs) [21].

AOPs are water treatment processes implemented at ambient temperature which involve generation of highly oxidative chemical species as decomposers of organic chemicals [22–25]. Ozone has recently received much attention in water treatment technology because of its high oxidation and disinfection potential. It is now widely assumed that ozone reacts in aqueous solution on various organic and inorganic compounds, either by a direct reaction of molecular ozone or through a radical type reaction involving $\cdot\text{OH}$ induced by the ozone decomposition in water [26]. However, ozone has a few disadvantages, such as relatively low solubility and stability in water, slow reaction with some organic compounds and low mineralization [27]. As

* Corresponding author. Tel.: +86 451 82291644/86283010;
fax: +86 451 82368074.

** Co-corresponding author. Tel.: +86 451 86282292/86283010;
fax: +86 451 82368074.

E-mail addresses: zhaolei99999@126.com (L. Zhao), majun@hit.edu.cn (J. Ma).

a promising AOP for water treatment, catalytic ozonation has been investigated for greater ozonation process efficiency and to optimise economic efficiency [28,29].

The primary objective of this study was to examine the degradation efficiency of NB in aqueous solution by the processes of ozone alone and ozone/ceramic honeycomb. NB was selected due to its refractory nature to conventional water treatment. The degradation products were identified by GC/MS and IC analysis, and possible pathways of oxidation were proposed.

2. Materials and methods

2.1. Materials and reagents

NB with purity of 99.80%, obtained from Beijing Chemical Industrial Factory, was redistilled at 210.8 °C under atmospheric pressure before use. *Tert*-butanol was purchased from Beijing Chemical Co. Ltd., and used without further purification. Solutions were prepared with twice-distilled water. Other chemicals used in these experiments, such as sodium thiosulfate solution, potassium iodide and so on, were all analytical-grade reagents.

Ceramic honeycombs with the constituent of 2MgO–2Al₂O₃–5SiO₂ were purchased from Shanghai Pengyi Material Co. Ltd. The monolithic honeycomb was cylindrical (50 mm in diameter and 50 mm in length), and the cell density was 400 cells per square inch. The monolith pieces were cleaned by boiling them in twice-distilled water for 90 min, followed by overnight drying at 240 °C.

2.2. Ozonation procedure

Experiments were carried out in a cylindrical reactor (inside diameter of 50 mm, the practical length of 1.5 m and the volume of 3 L) made of stainless steel (shown in Fig. 1), which was shielded to control reaction temperature constantly at 20 ± 1 °C using a thermostatic bath (DC-3005A, Ningbo Haishutianheng Apparatus Factory, China) and flow through a surrounding water jacket. Ozone was produced from pure oxygen (Harbin Gas Co. Ltd., 99.999%, China) through XFZ-5 ozone generator (Qinghua Tongli, China) at a power setting of 40 W, and was subsequently fed into the ozonation reactor to

contact thoroughly with water samples through a porous titanium sand plate at the bottom of the reactor. Before the experimental operation, the reactor was pre-ozonated for 4 min to satisfy any ozone demand in the column and then the column was washed several times with twice-distilled water to exclude possible side effects. In the ozonation tests, the model water (3 L), preparing by spiking 10 mg L⁻¹ NB in twice-distilled water, was pumped into the column by means of an MP-20R magnetic pump (Shanghai Xishan Pump Co. Ltd., China) and then circulated at a rate of approximately 2 L min⁻¹. The ceramic honeycomb catalysts were fed into the column by taking off its base. The ozonation time was controlled at 4 min for all the samples. Water samples were taken from the contactor column at various reaction times to analyze the residual concentration of NB. The oxidation reaction was stopped by the addition of a small amount of sodium thiosulphate solution.

2.3. Analytical methods

The concentration of NB in reaction process was determined by high performance liquid chromatography (HPLC) using a Shimadzu Co. (LC-10AT) instrument equipped with a UV detector and ODS-18 column. The mobile phase was a mixture of methanol and water (70:30 v/v), and the flow rate was set to 1 mL min⁻¹. The concentration of ozone in the gas, including inlet and offgas ozone concentration, was analyzed by the iodometric method [30]. The concentration of residual ozone in aqueous solution was measured by spectrophotometer using the indigo method [31].

Mineralization of pollutant was monitored for total organic carbon (TOC) removal, which was determined with TOC analyser (P/N 638-91062-33, Shimadzu Co., Japan). The UV-vis absorption spectra of NB solutions were monitored by a UV-vis spectrophotometer (UV-2501PC, Shimadzu Co., Japan).

A gas chromatographic and mass spectrometric analysis system (GC/MS, 6890GC/5973MS, Agilent, USA) with 30 m × 0.25 μm × 0.25 mm DB-5 column was used to identify the degradation products. The chromatographic conditions were the following: the initial column temperature was held for 2 min at 60 °C, ramped at 5 °C min⁻¹ to 200 °C, and then ramped at 20 °C min⁻¹ to 280 °C. Ultra pure helium was used as the carrier gas at a velocity of 1.0 mL min⁻¹. Before being subjected to GC/MS analysis, the samples were enriched by means of solid-phase extraction (SPE) with HPD-100/300/600 absorbent resins (Cangzhou Chemical Co. Ltd., China) after ozonation. The enrichment column was eluted by ether. Elution rate was 2 mL min⁻¹, and then dehydrated by anhydrous sodium sulfate for 5 min. The filtrate was then concentrated to 1 mL using a K-D concentrator. A splitless injector was used with a column head pressure of 10 psi (69 kPa), and extract of 2 μL was subjected to GC/MS determination.

Ion Chromatography (IC, CDD-6A, Shimadzu Co., Japan) was used to identify organic acid (eluent: 2.5 mmol L⁻¹ tris-hydroxymethyl-aminomethane, 2.5 mmol L⁻¹ phthalic acid)

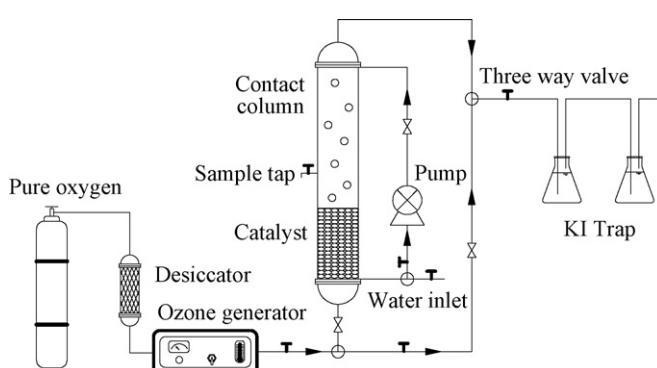


Fig. 1. Schematic of experimental apparatus for ozonation.

and inorganic nitrogen species (eluent: 8.0 mmol L⁻¹ *p*-hydroxybenzoic acid, 3.2 mmol L⁻¹ 1,3-bis[tris(hydroxymethyl)methylamino]propane, 50 mmol L⁻¹ boric acid).

3. Results and discussion

3.1. Degradation rate of NB in the different processes

The experiment investigated the degradation rates of the three different processes, including ozonation alone, ozonation/ceramic honeycomb and adsorption of ceramic honeycomb catalyst. The results are shown in Fig. 2. It was found that the concentration of NB generally decreased with increasing reaction time both in the systems of ozonation alone and catalytic ozonation, and NB removal obtained from 45.9% in the process of ozonation alone to 69.5% in the presence of ceramic honeycombs. These results suggested that the degradation rate of NB was enhanced on account of the catalytic activity of ceramic honeycombs. Under the same operating conditions, the adsorption removal of NB on the catalyst surface only caused 2.0% degradation, which appeared negligible compared to the rates of removal for the two ozonation systems in 20 min reaction. The lower rate in terms of the adsorption might not be attributed to an increased level of NB decomposition.

The chemistry of ozone in aqueous solution is complex. It is now widely assumed that ozone reacted in aqueous solution on various organic and inorganic compounds, either by direct, selective reactions of molecular ozone or through a radical type reaction involving •OH induced by ozone decomposition in water [26,27]. •OH was a less selective and more powerful oxidant than molecular ozone, and it was one of the most reactive free radicals and one of the strongest oxidants [32]. The rate at which •OH reacts with organic molecules is usually in the order of 10⁶–10⁹ M⁻¹ s⁻¹ [33].

In this study, NB could be selected as a probe compound for •OH measurement, which could trace •OH, because of its low

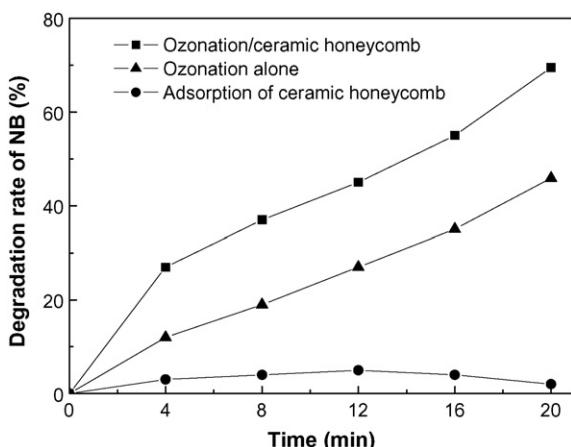


Fig. 2. Comparison of degradation rates in different processes. Experimental conditions: temperature, 20 ± 1 °C; pH of ozonation alone: 6.80–5.88; pH of ozonation/ceramic honeycomb: 6.80–4.58; initial nitrobenzene concentration: 10 mg L⁻¹; number of ceramic honeycombs used: 5 blocks; total ozone applied: 5.0 mg L⁻¹.

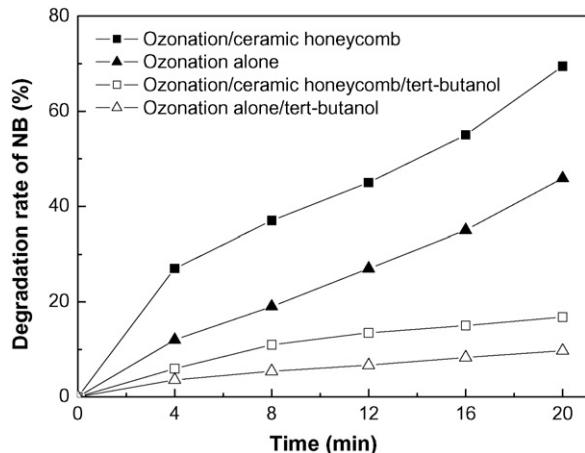


Fig. 3. Effect of *tert*-butanol on the degradation of nitrobenzene. Experimental conditions: temperate, 20 ± 1 °C; pH of ozonation alone: 6.80–5.88; pH of ozonation/ceramic honeycomb: 6.80–4.58; pH of ozonation alone/*tert*-butanol: 6.80–5.26; pH of ozonation/ceramic honeycomb/*tert*-butanol: 6.80–4.47; initial NB concentration: 10 mg L⁻¹; number of ceramic honeycombs used: 5 blocks; initial *tert*-butanol concentration 10 mg L⁻¹; total ozone applied: 5.0 mg L⁻¹.

reaction rate constant with ozone alone ($K_{NB-O_3} = 0.09 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$), but it could be degraded by •OH due to its high reactivity with •OH ($K_{NB-\bullet OH} = 2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [34]. Therefore, the phenomenon of this experiment suggested that ceramic honeycomb catalyst might promote initiation of •OH, which increased the degree of decomposition of the model compound.

3.2. Effect of *tert*-butanol on the degradation rate of NB

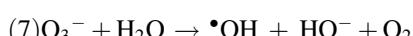
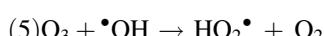
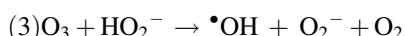
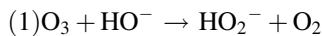
In order to confirm the mechanism of ceramic honeycomb-catalyzed ozonation, the experiment compared the degradation rate of NB obtained in the presence of *tert*-butanol with the rate in its absence, based on the aspect of competitive reaction. Fig. 3 shows the experimental results.

It is seen in Fig. 3 that the addition of *tert*-butanol in aqueous solution had a remarkable influence on the degradation rate during catalytic ozonation, resulting in a significant reduction of NB removal from 69.5% to 16.8% even at the low initial *tert*-butanol concentration (10 mg L⁻¹). In the case of ozone alone, *tert*-butanol also retarded the degradation of NB from 45.9% to 9.7%.

It is well known that *tert*-butanol is a stronger radical scavenger due to its higher reaction rate constant with •OH ($K_{TB-\bullet OH} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [35], compared to $3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ with ozone alone [36]. *Ter*-butanol reacts with •OH and generates inert intermediates, thus causing termination of the radical chain reaction. Therefore, it is a suitable indicator for radical type reaction. Otherwise, comparing the reaction rate constant $K_{NB-\bullet OH}$ with $K_{TB-\bullet OH}$, it is found that the former is much lower than the latter. *Ter*-butanol, being a radical scavenger, would trap competitively •OH in aqueous solution and became the main disadvantage of all oxidative degradation processes based on •OH reactions. Just from the results of this experiment, it was very clear that NB was oxidized primarily by

$\cdot\text{OH}$ in both the systems of ozonation alone and ozonation/ceramic honeycomb.

As far as ozonation alone was concerned, the reason why the presence of radical scavengers in water could also cause the total inhibition of the free radical chain reaction was the following. Molecular ozone, due to its resonance structure, could react as a dipole, an electrophilic or nucleophilic agent. As a result of its high reactivity, ozone was very unstable in water. The half-life time of molecular ozone varied from a few seconds up to few minutes and depended on pH, water temperature and so on [27,35]. Ozone decomposition in aqueous solution developed through the formation of $\cdot\text{OH}$ and proceeded through the following chain reaction [37]:



Obviously, HO^- ion had the fundamental role of initiator in reaction mechanism. Thus, the pH value of the solution remarkably influences ozone decomposition in water. Under the experimental conditions of temperature $20 \pm 1^\circ\text{C}$ and initial pH 6.80, ozone alone reacted with NB mostly through a radical type reaction involving $\cdot\text{OH}$ induced by the ozone self-decomposition in aqueous solution. So *tert*-butanol consumed $\cdot\text{OH}$ without the regeneration of the radical chain reaction and reduced similarly the degradation rate of the ozonation alone system.

3.3. Removal of TOC in the different processes

Ozone was used for many different purposes such as: disinfection and algal control, taste, odour and colour control, oxidation of inorganic pollutants (iron, manganese), oxidation of organic micro- and macropollutants as well as for the improvement of coagulation [27]. Interest in the use of ozone for drinking water treatment has been steadily increasing over the last several years in countries around the world due to its high oxidation potential [26,38]. However, ozonation has a few disadvantages, one of which is not to cause the complete oxidation of organic compounds, specifically due to the refractory character of some pollutants such as NB. The study showed the removal of TOC in the processes of ozonation alone and ozonation/ceramic honeycomb (see Fig. 4).

Fig. 4 shows that catalytic ozonation is more effective than ozonation alone to remove TOC from water containing NB, 49.6% of the initial TOC was degraded in catalytic ozonation compared to 31.7% in ozonation alone with same total ozone applied 5.0 mg L^{-1} . As expected, the increase in ozone dose led

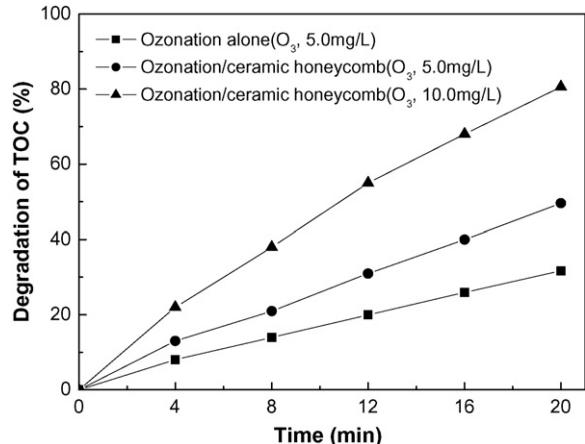


Fig. 4. Degradation of TOC in ozonation alone and catalytic ozonation. Experimental conditions: temperature, $20 \pm 1^\circ\text{C}$; pH of ozonation alone ($\text{O}_3, 5.0 \text{ mg L}^{-1}$): 6.80–5.88; pH of ozonation/ceramic honeycomb ($\text{O}_3, 5.0 \text{ mg L}^{-1}$): 6.80–4.58; pH of ozonation/ceramic honeycomb ($\text{O}_3, 10.0 \text{ mg L}^{-1}$): 6.80–3.96; initial NB concentration: 10 mg L^{-1} ; number of ceramic honeycombs used: 5 blocks.

to an increase in removal of TOC. Approximately 81.3% of initial TOC was removed after consumption of ozone 10.0 mg L^{-1} .

Ozonation alone has been shown to achieve a very limited mineralization of organic compounds in micropollutant removal in drinking water treatment or removal of refractory compounds in industrial effluents. Consequently, in order to achieve a complete mineralization of organic matter, various AOPs (such as $\text{O}_3/\text{H}_2\text{O}_2$, UV/O_3 , $\text{UV}/\text{H}_2\text{O}_2$, Fenton and UV/Fenton reagents, photocatalytic oxidation with TiO_2 , wet air oxidation, electron beam, catalytic ozonation) have been investigated as potential methods for degrading organic compounds. The above result, that greater TOC abatement is achieved in catalytic ozonation system, suggested that the ozonation/ceramic honeycomb system, as an AOP, could induce a distinct increase of mineralizing capability via decomposition of ozone and generation of $\cdot\text{OH}$. Moreover, the ability of the radical initiation would be enhanced by increasing the ozone dosages applied.

Comparing the reduction of TOC (Fig. 4) with the degradation rate of NB (Fig. 2) in the process of ozonation/ceramic honeycomb, it was found that the removal of TOC was lower than the disappearance of NB, indicating that NB has been converted mostly into carbon dioxide and water, and the intermediates were formed via the degradation of the initial compound in the oxidation process.

3.4. UV spectra of NB solution

Fig. 5 exhibits the typical UV-vis spectra of the treated NB solution at an initial NB concentration of 10 mg L^{-1} . The samples were treated for 0, 4, 8, 12, 16, and 20 min reaction. The characteristic absorption band of NB was at 268 nm.

As showed in Table 2, the absorption band at 268 nm decreased and shifted to a shorter wavelength as reaction time increased, whereas an absorption band at 200–220 nm was

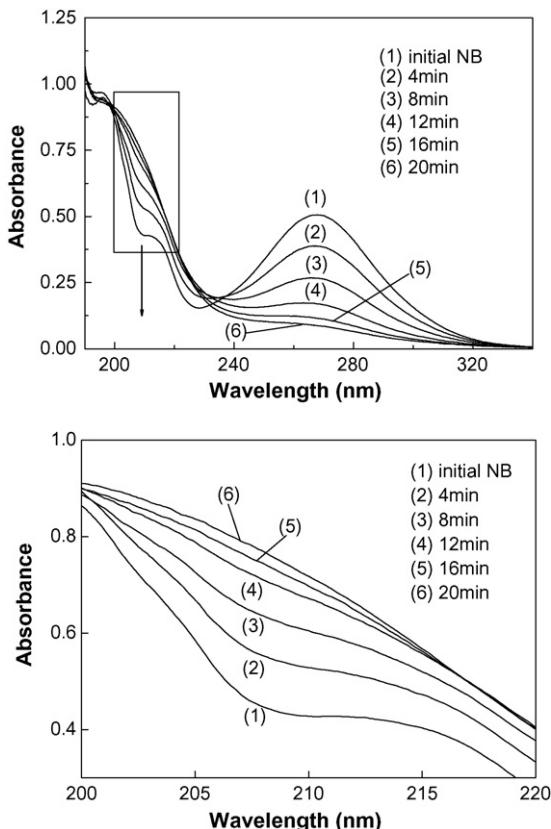


Fig. 5. UV spectra initially and after catalytic ozonation. Experimental conditions: temperature, $20 \pm 1^\circ\text{C}$; pH: 6.80–4.58; initial NB concentration: 10 mg L^{-1} ; number of ceramic honeycombs used: 5 blocks; total ozone applied: 5.0 mg L^{-1} .

formed and the band increased with reaction time to 20 min. The evolution of the absorption spectra, as shown in Fig. 5, demonstrated the degradation of NB and the formation of reaction products. Since the characteristic absorption bands of organic acids and aromatic compounds were within 200–220 nm, the absorption spectra suggested that carboxylic acids and aromatic compounds were predominant oxidative products of NB by catalytic ozonation. The formation of acids was also confirmed by the substantial decrease of pH value from initial 6.80 to 4.58 during the catalytic ozonation.

3.5. Analysis of the oxidation products of NB

The main possible points of chemical oxidant introduction during water treatment were pre-oxidation, intermediate oxidation and final disinfection. Generally, pre-oxidation was applied for the elimination of inorganic compounds, colour, taste, odour, turbidity and suspended solids. Intermediate oxidation had the aim of the degradation of micropollutants, the removal of trihalomethane precursors and increase of biodegradability [27,38]. Yet, as pointed out above, degradation was seldom complete in respect that numerous undesired by-products could generally be formed from the reaction of ozone and $\cdot\text{OH}$ with water matrix components [39–43] and remain after oxidation, including numerous organic and some inorganic species. In drinking water treatment, the problem of by-product formation has become even more prominent because ozonation is usually followed by biological filtration, partly oxidized organic compounds could decide whether be mineralized microbiologically or not, and might cause several

Table 1

The ozonation products of NB by GC/MS and IC (*) (initial NB concentration: 10 mg L^{-1} ; total ozone applied: 5.0 mg L^{-1} ; pH: 6.80–4.58)

nitrobenzene	<i>p</i> -nitrophenol	<i>m</i> -nitrophenol	<i>o</i> -nitrophenol	phenol
4-nitrocatechol	1,2,3-trihydroxy-5-nitrobenzene	hydroquinone	<i>p</i> -quinone	* maleic acid
				*
malonic acid	oxalic acid	acetic acid	nitrate ion	

problems such as a bacterial regrowth in the distribution network and/or an increase in mutagenic activity. Naturally, knowledge of both the nature of the by-products and the degradation pathway of pollution are of prime importance to ensure an efficient catalytic ozonation process [38]. In order to clarify the pathways of NB degradation, the experiment detected the degradation intermediates in the process of ozonation/ceramic honeycomb by GC/MS and IC. The results are summarized in Table 1.

Table 1 shows the degradation intermediates of NB. Nitrophenol, phenol, 4-nitrocatechol, 1,2,3-trihydroxy-5-nitrobenzene, malonic acid and acetic acid are the main products of NB degradation by the catalytic ozonation system. As the same time, NO_3^- , maleic acid and oxalic acid were detected by IC and confirmed according to the retention time. It was ascertained that *p*-quinones were formed during the ozonation of NB catalyzed by ceramic honeycombs. Moreover, some of

these quinones and their derivatives were very easily oxidised during the further ozonation and were no longer identified in the solution at the prolonged stages of ozonation. This phenomenon was responsible for the colour changes during the early stage of the reaction. The colour of the reaction mixture disappeared towards the end of the selected treatment time [44]. From the results of GC/MS analysis, *p*-nitrophenol, as one of the oxidation products, was dominant from peak height proportion in the intermediates. In order to further clarify the degradation pathways of NB by catalytic ozonation, *p*-nitrophenol was chosen to investigate the degradation products in catalytic ozonation process.

According to the results obtained, as shown in Table 2, the main aromatic intermediates detected in this work were hydroxylated products and their derivatives, including 4-nitrocatechol, 1,2,3-trihydroxy-5-nitrobenzene, hydroquinone, *p*-quinone and acetic acid, which were similar to those observed

Table 2

GC/MS data for identification of ozonation products of *p*-nitrophenol (experimental conditions: temperature, $20 \pm 1^\circ\text{C}$; pH: 6.80–5.32; initial *p*-nitrophenol concentration: 10 mg L^{-1} ; number of ceramic honeycombs used: 5 blocks; total ozone applied: 5.0 mg L^{-1})

Compound	Chemical structure	Molecular weight (<i>m/z</i>)	Mass of predominant ions in fragmentation pattern	Retention time (min)
<i>p</i> -Nitrophenol		139	139 (M^+), 109, 93, 81, 65, 53, 39	19.385
Hydroquinone		110	110 (M^+), 81, 69, 63, 54, 39	18.657
<i>p</i> -Quinone		108	108 (M^+), 82, 69, 54, 38, 32	10.055
4-Nitrocatechol		155	155 (M^+), 138, 109, 97, 81, 53, 39	18.933
1,2,3-Trihydroxy-5-nitrobenzene		171	171 (M^+), 154, 137, 120, 91, 75	18.785
Acetic acid		60	60 (M^+), 45, 43, 29, 18, 15	20.143

in photodegradation experiments, confirming that $\cdot\text{OH}$ oxidation was the major reaction pathway in the present catalytic ozonation [43,45–47]. The addition of a hydroxyl group to the aromatic ring was a dominating reaction in the first part of the degradation. Furthermore, as discussed by many authors, the final reaction by-products of *p*-nitrophenol degradation by ozonation, such as oxalic acid, nitrate ion and maleic acid were identified in the solution [44,48–50].

3.6. Proposed pathway for NB degradation

Based on the products analysis by GC/MS and IC, possible oxidation pathways for the NB degradation were proposed and illustrated in Fig. 6.

The catalyzed ozonation of the NB seemed to occur in several steps as follows: the hydroxylation of aromatic ring, the mineralization of organic nitrogen, the transformation of aromatics to aliphatics by destruction of ring structures and the oxidation of the aliphatic chains. The hydroxylation of the aromatic ring was the most important process [46]. Due to the predominant high redox potential of $\cdot\text{OH}$ ($E_0 = 2.8$ V), generated by the heterogeneous surface of the catalyst, $\cdot\text{OH}$ played the most crucial role in the degradation of NB and its decomposition products [16]. The reaction mechanism of $\cdot\text{OH}$ with the aromatic compounds is well known [51–53], consisting of an electrophilic addition to the aromatic ring with the formation of a hydroxylated radical [54]. Therefore, at first, $\cdot\text{OH}$ could attack the NB molecule, resulting in the occurrence of electron transfer and denitration, and the formation of phenyl radicals and nitrophenyl radicals [21]. However, the next interaction of these radicals might undergo different reactions according to the position of impact.

On the one hand, $\cdot\text{OH}$ could easily attack the benzene ring of nitrophenyl radicals at the carbon carrying a nitro-group as well as α -, β -or/and γ -carbons via electrophilic addition. If the attacks occurred at α -, β - and γ -carbons, as found previously, *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol would be formed while the protons are eliminated from the new adducts [7], and the formation of 4-nitrocatechol might be explained by the electrophilic attack of $\cdot\text{OH}$ on the *ortho* position of *p*-nitrophenol and *m*-nitrophenol.

Simultaneously, if $\cdot\text{OH}$ attacked the carbon carrying a nitro-group, phenol radicals and/or its derivatives, such as hydroquinone and *p*-quinones, would be generated and nitrate ions released by the radical addition–elimination. The previous research found that hydroquinone formation with a simultaneous cleavage of nitro-group was also detected during aromatic nuclear hydroxylation. It is well known that hydroquinone is very easily oxidised to *p*-quinones [44], thus it is probably formed by reaction of $\cdot\text{OH}$, which is also powerful oxidizing agents [54].

Among the by-products, *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol, resulting from aromatic nuclear hydroxylation of NB, the further attack of the electrophilic radical $\cdot\text{OH}$ occurred at the ring positions activated by the presence of the two substituents. The phenolic $-\text{OH}$ group was electron-donating for the electrophilic aromatic substitution, while the $-\text{NO}_2$ group was electron-withdrawing. The electron-donating substituents increased the electron density at the *ortho* and *para* positions while the electron-withdrawing substituents were strongly deactivating and *meta* directing. When both the substituents ($-\text{OH}$ and $-\text{NO}_2$) were present, the electrophilic attack would occur preferentially in *ortho* and *para* positions with respect to the $-\text{OH}$ group [44,46]. In a word, the activated positions in the ring of the three nitrophenol isomers decided the nature and properties of degradation products.

In the presence of *o*-nitrophenol or *m*-nitrophenol, $\cdot\text{OH}$ might attach to the *ortho* and *para* positions to form 3-nitrocatechol and 1,4-dihydroxy-2-nitrobenzene or 3-nitrocatechol, 4-nitrocatechol and 1,4-dihydroxy-2-nitrobenzene, respectively. In the case of *p*-nitrophenol only 4-nitrocatechol could be obtained. The phenomenon revealed that the attack of $\cdot\text{OH}$ followed the expected pattern of the electrophilic substitution [46]. Studies of the degradation of *p*-nitrophenol by Fenton reaction have determined that $\cdot\text{OH}$ could interact with solution-phase *p*-nitrophenol to form 4-nitrocatecho [55]. Therefore, some of the 4-nitrocatecho produced in the system might also occur by reaction with solution-phase nitrophenolate ion [45].

Likewise, the next stage of the degradation of *p*-nitrophenol implied the addition of $\cdot\text{OH}$ to benzene ring to yield 1,2,3-trihydroxy-5-nitrobenzene through aromatic nuclear hydroxylation of 4-nitrocatechol, as illustrated by the formation of compound 1,2,3-trihydroxy-5-nitrobenzene by hydroxylation of *p*-nitrophenol during the photo-Fenton process [55] and the electro-Fenton method [54]. The possibility also existed of a direct attack of the $\cdot\text{OH}$ at the *meta* position carbon carrying the nitro-group of 3-nitrocatechol and 1,4-dihydroxy-2-nitrobenzene with resultant 1,2,4-trihydroxy-6-nitrobenzene formation. Then these trihydroxynitrobenzene isomers as intermediate compounds might be oxidized into 1,2,3,4-tetrahydroxy-5-nitrobenzene through the electrophilic attack of $\cdot\text{OH}$.

On the other hand, phenyl radicals could also be transformed into phenol through $\cdot\text{OH}$ attack. The formation of phenol radicals in aqueous solutions was possible as a result of the further oxidation, derived from $\cdot\text{OH}$, of phenol and *p*-nitrophenol. Accordingly the addition of $\cdot\text{OH}$ to *p*-nitrophenol and phenol radicals resulted in the formations of hydroquinone, hydroquinone radicals and 1,2,4-trihydroxybenzene. It was proposed that $\cdot\text{OH}$ abstracted hydrogen from solution-phase nitrophenolate ion, leading to denitration and $\cdot\text{OH}$ substitution to form hydroquinone [45]. In fact, oxidation of phenol led to hydroquinone, which could be further degraded to either *p*-quinones, through abstraction of two hydrogens, or 1,2,4-trihydroxybenzene, by the reactions of hydrogen abstraction and addition of $\cdot\text{OH}$ [56].

The study indicated that both hydroquinone and 4-nitrocatechol would react further with $\cdot\text{OH}$ to form 1,2,4-trihydroxybenzene, followed by ring cleavage and eventual mineralization [45]. However, this intermediate was detected only under not much oxidizing conditions. It is known that the C–C bonds between the adjacent hydroxyl groups are destabilized due to the strong electrophilic effect of hydroxyl and nitro groups [54]. Consequently these bonds easily

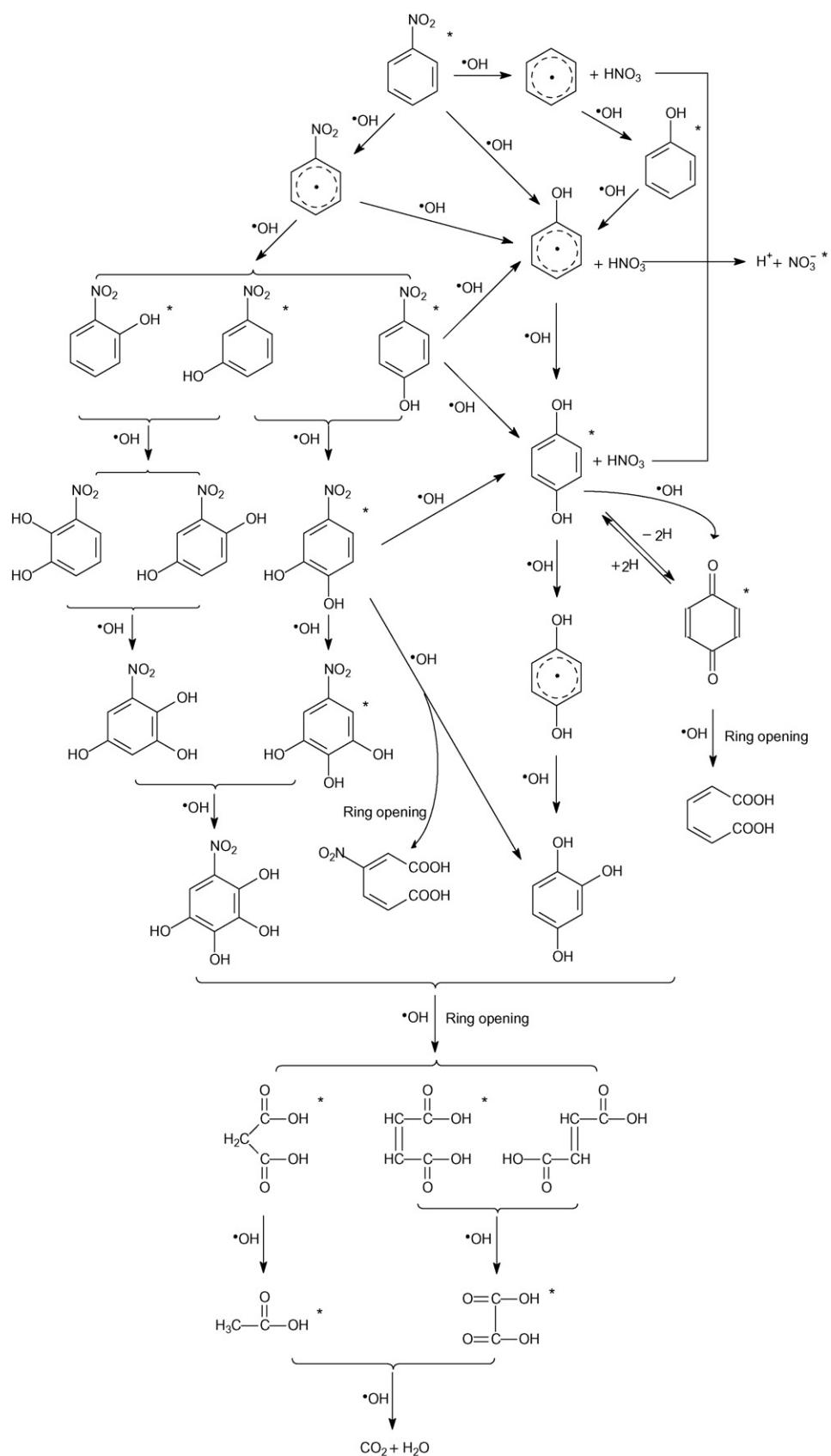


Fig. 6. General reaction pathway proposed for nitrobenzene degradation by catalytic ozonation (the compounds with an asterisk have been detected).

underwent oxidative ring opening reactions leading to aliphatic compounds, and the ring cleavage in the presence of oxidative conditions was so rapid that no detectable amount of 1,2,4-trihydroxybenzene accumulated in the system [45,46]. Contrarily, Mehmet et al. observed that the decrease of *p*-nitrocatechol was accompanied by an increase of 1,2,4-trihydroxybenzene [54]. According to the previous studies, the reaction of hydroquinone with •OH would produce additional HO-substituted benzene such as 1,2,4-trihydroxybenzene. The products would be further oxidized to cleave the aromatic ring, form aliphatic acids, and finally be converted into carbon dioxide [57].

In addition, •OH, which could take different attacking approaches beyond those mentioned above, might be coupled with organic substances in some complex way. The direct reaction of •OH initiated by ozone decomposition with 4-nitrocatechol mainly gave nitromuconic acid [44,58] and hydroquinone as primary products. The formation of nitromuconic acid was achieved in the catalytic ozonation by the selective attack of •OH on the C–C bonds between the adjacent hydroxyl groups. Further degradations could occur to produce muconic acid in case that •OH reacted with *p*-quinones, which followed by successive oxidations of hydroquinone by •OH [44].

Furthermore, reactions of the primary intermediates mentioned above with •OH led to benzene ring cleavage and formation of oxygenated aliphatic compounds, which could be degraded to carboxylic acids via alcohols, aldehydes or ketones (from quinones), such as maleic acid, malonic acid, oxalic acid and acetic acid identified in this study. For example, destruction of NB with release of NO_3^- , *p*-quinones and 1,2,4-trihydroxybenzene gave maleic and fumaric acids [56]. The fact that these organic diacids were not detected under photocatalytic conditions pointed to a rapid mineralization to CO_2 of both compounds [56]. IC analyses of carboxylic acid, which formed from oxidative cleavage of hydroxylated aromatic compounds 1,2,4-trihydroxybenzene and 1,2,3-trihydroxy-5-nitrobenzene, revealed maleic acid as the major by-product of these reactions and the presence of fumaric and oxalic acids at very low concentration [54]. These observations were in agreement with the previous studies [56,59–61].

Thus, for the experimental systems, maleic and fumaric acid were directly mineralized to CO_2 via oxalic acid, being accelerated by reaction of such diacids and its intermediates with •OH [62]. Moreover, malonic acid would be converted into acetic acid by further oxidation initiated by •OH. Finally, these aliphatic by-products would be mineralized to CO_2 and H_2O .

As far as the nitro-group is concerned, NO_3^- was the major product. This phenomenon could be explained by the cleavage of the nitro-group from aromatic compounds and nitrated aliphatic intermediates because the nitro-group in nitroaromatics is a very good leaving group which can be easily eliminated. Therefore, in the present oxidation process, phenol formed via denitration and hydroquinone formed from *p*-nitrophenol, favouring the electrophilic substitution of •OH at the *para* position with respect to the hydroxyl group. The formation of nitrate was a result of mineralization of

organically bounded nitrogen during the NB ozonation catalyzed by ceramic honeycomb.

From the degradation intermediates of NB and *p*-nitrophenol, destruction of aromatic structures, hydroxylation and nitrogen mineralization were involved in the ozonation process, and organic acids were formed as a result of the opening of aromatic ring. The chemical transformations might enhance the biodegradability of nitroaromatic compounds, suggesting that catalytic ozonation could be applied for biodegradability improvement and detoxification as an effective treatment method.

4. Conclusion

This study demonstrated that the presence of ceramic honeycomb could improve the reaction efficiency of ozonation for the degradation of NB, and NB was oxidized primarily by •OH in both the systems of ozonation alone and ozonation/ceramic honeycomb. The combined use of ozone and ceramic honeycomb catalyst led to a conspicuous TOC conversion in 20 min, which compared favorably to the absence of the catalyst. It also could be estimated that the advanced TOC removal of the ozonation/ceramic honeycomb was due to the accelerating capability of the formation of •OH, initiated by the heterogeneous surface of catalyst. The major intermediary degradation products, including nitrophenols, phenol, 4-nitrocatechol, hydroquinone, *p*-quinone, 1,2,3-trihydroxy-5-nitrobenzene, maleic acid, malonic acid, oxalic acid, acetic acid and nitrate ion, were unequivocally identified and confirmed by GC/MS and IC methods. A possible reaction pathway was proposed due to the mechanism of fast and non-selective •OH oxidation, with the •OH formed by decomposition of the ozone molecule and accelerated by the presence of ceramic honeycomb in aqueous solution.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China for the financial support of this study (Project Number: 50378028).

References

- [1] Y. Mu, H.-Q. Yu, J.-C. Zheng, S.-J. Zhang, G.-P. Sheng, Chemosphere 54 (2004) 789.
- [2] J.-S. Zhao, O.P. Ward, P. Lubicki, J.D. Cross, P. Huck, Biotechnol. Bioeng. 73 (2001) 306.
- [3] S. Contreras, M. Rodríguez, E. Chamarro, S. Esplugas, J. Photochem. Photobiol. A: Chem. 142 (2001) 79.
- [4] J. Sarasa, M.P. Roche, M.P. Ormad, E. Gimeno, A. Puig, J.L. Ovelleiro, Water Res. 32 (1998) 2721.
- [5] L.S. Bell, J.F. Devlin, R.W. Gillham, P.J. Binning, J. Contam. Hydrol. 66 (2003) 201.
- [6] M. Rodriguez, V. Timokhin, F. Michl, S. Contreras, J. Gimenez, S. Esplugas, Catal. Today 76 (2002) 291.
- [7] D.S. Bhatkhande, V.G. Pangarkar, A.A.C.M. Beenackers, Water Res. 37 (2003) 1223.
- [8] D.R. Hartter, in: D.E. Rickett (Ed.), Toxicity of Nitroaromatic Compounds, Hemisphere Publishing, Washington, DC, 1984, p. 1.

[9] P.H. Howard, Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Lewis Publishers, Chelsea, Michigan, 1989, pp. 421.

[10] S.P. Wang, H.J. Chen, *J. Chromatogr. A* 979 (2002) 439.

[11] S.H. Zahm, D.D. Weisenburger, P.A. Babbitt, R.C. Saal, J.B. Vaught, A. Blair, *Am. J. Public Health* 82 (1992) 990.

[12] D. Bahnemann, in: O. Hutzinger, P. Boule (Eds.), *The Handbook of Environmental Chemistry*, Springer, Berlin, 1999, p. 285.

[13] D.S. Bhatkhande, V.G. Pangarkar, A.A. Beenackers, *J. Chem. Technol. Biotechnol.* 77 (2001) 102.

[14] R. Dillert, M. Brandt, I. Fornefett, U. Siebers, D. Bahnemann, *Chemosphere* 30 (1995) 2333.

[15] M. Rodríguez, A. Kirchner, S. Contreras, E. Chamarro, S. Esplugas, *J. Photochem. Photobiol. A: Chem.* 133 (2000) 123.

[16] S.J. Zhang, S.H. Feng, H.Q. Yu, Q.R. Li, *J. Environ. Sci.* 16 (2004) 364.

[17] T. Gorontzy, J. Kuver, K.H. Blotevogel, *J. Gen. Microbiol.* 139 (1993) 1331.

[18] D. Mansuy, P. Beaune, T. Crestell, C. Bacot, J.C. Chottard, P. Gans, *Eur. J. Biochem.* 86 (1978) 573.

[19] A. Schackmann, R. Müller, *Appl. Microbiol. Biotechnol.* 34 (1991) 809.

[20] C.Z. Thompson, L.E. Hill, J.K. Epp, G.S. Probst, *Environ. Mutagen.* 5 (1983) 803.

[21] Q.-R. Li, C.-Z. Gu, Y. Di, H. Yin, J.-Y. Zhang, *J. Hazard. Mater. B* 133 (2006) 68.

[22] J.H. Carey, *Water Poll. Res. J. Can.* 27 (1992) 1.

[23] W.H. Glaze, F. Beltran, T. Tuukkanen, J.W. Kang, *Water Poll. Res. J. Can.* 27 (1992) 23.

[24] W.H. Glaze, J.W. Kang, D.H. Chapin, *Ozone Sci. Eng.* 9 (1987) 335.

[25] O. Legrini, E. Oliveros, A.M. Braun, *Chem. Rev.* 93 (1993) 671.

[26] B. Legube, V.L.N. Karpel, *Catal. Today* 53 (1999) 61.

[27] B. Kasprzyk-Hordern, M. Ziółek, J. Nawrocki, *Appl. Catal. B: Environ.* 46 (2003) 639.

[28] M. Ernst, F. Lurot, J.-C. Schrotter, *Appl. Catal. B: Environ.* 47 (2004) 15.

[29] J.-S. Park, H. Choi, J. Cho, *Water Res.* 38 (2004) 2284.

[30] K.L. Rakness, G. Gordon, B. Langlais, W. Masschelein, N. Matsumoto, Y. Richard, C.M. Robson, I. Somiya, *Ozone Sci. Eng.* 18 (1996) 209.

[31] H. Bader, J. Hoigné, *Water Res.* 15 (1981) 449.

[32] C.P. Huang, C. Dong, Z. Tang, *Waste Manage.* 13 (1993) 361.

[33] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, *Catal. Today* 53 (1999) 51.

[34] J. Hoigné, H. Bader, *Water Res.* 10 (1976) 377.

[35] G. Bablon, W.D. Bellamy, M.M. Bourbigot, in: B. Langlais, D.A. Reckhow, D.R. Brink (Eds.), *Ozone in Water Treatment: Application and Engineering*, Lewis Publishers, Chelsea, Michigan, USA, 1991 , p. 11.

[36] J. Hoigné, H. Bader, *Water Res.* 17 (1983) 173.

[37] W.K. Joon, M.R. Hoffmann, *Environ. Sci. Technol.* 32 (1998) 3194.

[38] V. Camel, A. Bermond, *Water Res.* 32 (1998) 3208.

[39] R.J. Miltner, H.M. Shukairy, R.S. Summers, *J. Am. Water Works. Ass.* 84 (1992) 53.

[40] S.D. Richardson, J.A.D. Thruston, T.V. Caughran, P.H. Chen, T.W. Collette, T.L. Floyd, K.M. Schenck, J.B.W. Lykins, G.R. Sun, G. Majetich, *Environ. Sci. Technol.* 33 (1999) 3378.

[41] S.D. Richardson, J.A.D. Thruston, T.V. Caughran, P.H. Chen, T.W. Collette, T.L. Floyd, K.M. Schenck, J.B.W. Lykins, G.R. Sun, G. Majetich, *Environ. Sci. Technol.* 33 (1999) 3368.

[42] U. von Gunten, *Water Res.* 37 (2003) 1443.

[43] M.H. Zhou, Z.C. Wu, J. Zhu, Q. Ye, J. Fu, *Chin. J. Catal.* 23 (2002) 276.

[44] A. Goi, M. Trapido, T. Tuukkanen, *Adv. Environ. Res.* 8 (2004) 303.

[45] M.S. Dieckmann, K.A. Gray, *Water Res.* 30 (1996) 1169.

[46] A. Di Paola, V. Augugliaro, L. Palmisano, G. Pantaleo, E. Savinov, *J. Photochem. Photobiol. A: Chem.* 155 (2003) 207.

[47] K. Tanaka, W. Luesaiwong, T. Hisanaga, *J. Mol. Catal. A: Chem.* 122 (1997) 67.

[48] A. Chauhan, A.K. Chakraborti, R.K. Jain, *Biochem. Biophys. Res. Commun.* 270 (2000) 733.

[49] M. Trapido, Y. Veressinina, J. Kallas, *Ozone Sci. Eng.* 32 (2001) 333.

[50] C.P. Yu, Y.H. Yu, *Ozone Sci. Eng.* 23 (2001) 303.

[51] M.K. Eberhardt, *J. Phys. Chem.* 81 (1977) 1051.

[52] M.A. Oturan, J. Pinson, *J. Phys. Chem.* 99 (1995) 13948.

[53] N.V. Raghavan, S. Steenken, *J. Am. Chem. Soc.* 102 (1980) 3495.

[54] A.O. Mehmet, P. Jose, C. Pascal, J.A. Aurel, *Environ. Sci. Technol.* 34 (2000) 3474.

[55] J. Kiwi, C. Pulgarin, P. Peringer, *Appl. Catal. B: Environ.* 3 (1994) 335.

[56] E. Brillas, E. Mur, R. Sauleda, L. Sánchez, J. Peral, X. Domènec, J. Casado, *Appl. Catal. B: Environ.* 16 (1998) 31.

[57] N. Chitose, S. Ueta, S. Seino, T.A. Yamamoto, *Chemosphere* 50 (2003) 1007.

[58] F.J. Beltrán, J. Rivas, P.M. Álvarez, M.A. Alonso, B. Acedo, *Ind. Eng. Chem. Res.* 38 (1999) 4189.

[59] N.B. Tahar, A. Savall, *J. Appl. Electrochem.* 29 (1999) 277.

[60] C. Cominellis, C. Pulgarin, *J. Appl. Electrochem.* 23 (1993) 108.

[61] P.L. Huston, J.J. Pigratello, *Water Res.* 33 (1999) 1238.

[62] R. Sauleda, E. Brillas, *Appl. Catal. B: Environ.* 29 (2001) 135.